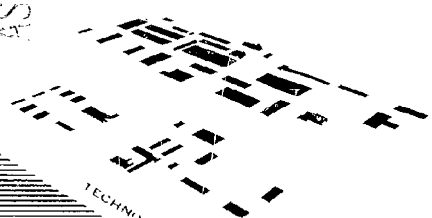
63 4-2

ARF

ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY



TECHNOLOGY CENTER

408 419

NOTE: Effective June 1, 1963, the name of Armour Research Foundation of Illinois Institute of Technology will change to IIT RESEARCH INSTITUTE.

Contract No. DA-11-ORD-022-3108

EMBRITTLEMENT OF METALS

BY ORGANIC LIQUIDS

ARF-B183-14
(Quarterly Report)

Commanding Officer
Frankford Arsenal
Philadelphia 37, Pennsylvania

ARMOUR RESEARCH FOUNDATION
of
ILLINOIS INSTITUTE OF TECHNOLOGY
Technology Center
Chicago 16, Illinois

Contract No. DA-11-ORD-022-3108

EMBRITTLEMENT OF METALS BY ORGANIC LIQUIDS

ARF-B183-14
(Quarterly Report)

March 1, 1963, to May 31, 1963

for

Commanding Officer
Frankford Arsenal
Philadelphia 37, Pennsylvania

Attention: Mr. J. M. McCaughey
Pitman-Dunn Laboratories

June 18, 1963

EMBRITTLEMENT OF METALS
BY ORGANIC LIQUIDS

ABSTRACT

About 200 liquids and solutions representative of 24 categories of organic and metallo-organic species have been chosen to test for embrittling capability on a high strength steel and a high strength aluminum alloy. Embrittlement is being measured in terms of loss of tensile strength and ductility, tendency to failure under sustained loads at the yield point and decrease in fatigue life under tension-tension stress conditions and deep machined notches. Thus far embrittlement clearly relevent to the existence of an organic liquid on the stressed surface has not been discovered.

TABLE OF CONTENTS

EMBRITTLEMENT OF METALS BY ORGANIC LIQUIDS

I. INTRODUCTION

This is the second quarterly report summarizing progress in one portion of the larger program entitled "Fracture of Metals," identified under Contract No. DA-11-ORD-022-3108. This report covers the period March 1, 1963, to May 31, 1963.

This portion of the program on "Fracture of Metals" is exploring the existence and nature of embrittlement which might be produced by exposure to organic liquids and tensile stresses. Since the published literature on this subject is fragmentary and ambiguous, the first steps in this program involve simple explorations for embrittlement with the objective of defining the groupings of organic species which can produce such effects. More detailed analysis of mechanism will follow upon a clearer appreciation of the scope and nature of the phenomenon. In this work, organic liquids will be defined as pure liquid species, miscible liquids, and solutions of solids in liquids. Embrittlement constitutes the premature incidence of cracking under continuously increasing load, static loading, or dynamic (cyclic) loading. "Premature" implies a lower load, a shorter time, or fewer cycles than would be expected for the material in air.

II. SCHEME OF EXPLORATION

The search for embrittlement could involve an almost infinite number of combinations of stress level, stress system, candidate materials, and candidate environments. Logic and prior experience must be applied to selecting the combinations of circumstances most likely to produce premature failure. Two test materials have been selected--a high-strength steel and a high-strength aluminum alloy. In both cases, the material and its state of heat treatment are known to be susceptible to embrittlement by stress-corrosion and low melting liquid metals.

The steel has a commercial designation of 300M and a nominal composition of 0.4% C, 1.6% Si, 0.75% Mn, 0.85% Cr, 1.85% Ni, 0.4% Mo, 0.08% V. This steel is being used in a heat-treated condition produced by quenching and tempering to give a yield strength of about 204,000 psi.

The commercial aluminum alloy designated 2024 has a nominal composition of 4.5% Cu, 1.5% Mg, 0.6% Mn and is being used in the age-hardened conditions termed T3 and T4, which are capable of yield strengths of 50,000 psi and 47,000 psi, respectively.

The program embraces three simple systems of mechanical stressing--tensile strength under continuously increasing load, static loading near the yield point, and cyclic loading (fatigue). Simple tensile testing involves flat sheet specimens with a 2-in. gage length. During the test at a strain rate of about 0.05 in. per minute, the gage section is swabbed generously with the candidate organic liquid. The full stress-strain curve to failure is recorded and final elongation measured.

The system for inducing delayed failure under static loading was described in the previous report. The present procedure is the same except for the use of an asbestos pad clipped to the tension surface and saturated with the candidate organic liquid. The pad acts as a wick and reservoir of reagent over the whole area of high tensile stress. Figure 1 illustrates the arrangement.

Figure 2 illustrates the type of edge-notched specimen used for tension-tension type of fatigue testing and the arrangement of pads, clips, and wrapping by which the candidate organic liquid was brought in contact with the notched region of the specimen. The notch itself was finished to 0.001 in. root radius with special files. Fatigue testing was done in a Baldwin fatigue machine operating at 1800 cpm. According to previous published work, this slow rate of cycling was more conducive to premature cracking in the presence of surfactants.

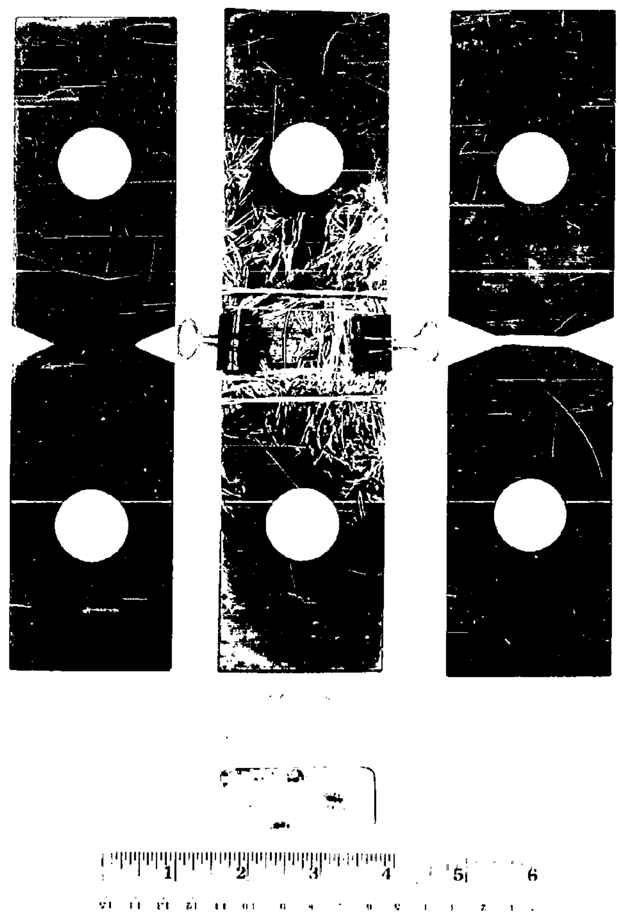
III. SUMMARY OF ORGANIC LIQUID CANDIDATES

The various selected candidates were applied to embrittlement tests in various conditions. Organic species which were naturally liquids at room temperature were used in that condition. Organic species which are solid

Neg. No. 25005

FIG. 1 - STATIC STRESSING SYSTEM

Stresses at the yield point of the test specimen. Asbestos pad clipped to tension side of the specimen and saturated with candidate embrittling liquid. The whole assembly is placed inside a glass bottle closed with a rubber gasketed steel cap. In the case of saline-base solutions the glass bottle is prerinsed with salt water to minimize evaporation from the pad.



Neg. No. 25006

FIG. 2 - ILLUSTRATION OF EDGE-NOTCHED SHEET SPECIMEN FOR TENSION-TENSION FATIGUE IN THE PRESENCE OF CANDIDATE ORGANIC EMBRITTLING LIQUIDS. Shows arrangement of liquid-saturated pads clipped to the fracture zone and wrapped to prevent volatilization. Character of fracture also shown.

at room temperature were dissolved in inert liquid solvents such as:

- Dibutyl carbitol
- Light white paraffin oil
- Dioctylphthalate
- Halocarbon oil
- Heavy white mineral oil

The strength of the solution was as concentrated as practical. This permitted 50% additions in some cases and only 1% in others.

Another set of liquids was prepared using a 5% NaCl water solution as a solvent. The saline solution base was chosen because it is aggressive against the oxide protective films on both steel and aluminum. By destroying the protective character of the oxide films, the soluble organic species should more easily arrive at the true metal surface. Of necessity the number of saline solutions was more limited because of the insolubility of many of the organic species. Both highly soluble and slightly soluble organic species were included in this group.

The organic species used in this investigation can be catalogued into the following groups:

- Organic acids
- Amines
- Alcohols
- Aldehydes
- Metal salts of organic acids
- Metal-organic compounds
- Halogenated organic compounds
- Organic acid amides
- Hydrocarbons
- Esters
- Ketones
- Organic phosphorus, sulfur, silicon compounds
- Organic ether
- Organic ketoximes
- Commercial organic surfactants

Organic acid anhydrides
Organic metaloxy compounds
Organic acid halides
Amines organic ethers
Amines alcohols
Metal organic esters
Metal organic alcohols
Amines esters
Alcohol ketones
Amines aldehyde
Silicon-metal organic compounds
Sulfo-metaloxy-alcohols

Table I lists the various members of these groups which have been included in the test program. To save cumbersome reuse of names, solvents, and concentrations, an identifying code has been applied and will be used to record test results.

IV. TENSILE BEHAVIOR OF Al 2024-T4

Almost every item in Table I has been used to swab the gage section of Al alloy test specimens during tensile testing. Beyond the yield point the oxide films should crack repeatedly and expose bare metal to the organic liquid. However, in no case was the stress-strain curve modified by the presence of an organic liquid film. This includes yield and ultimate strengths, rate of strain hardening, and total elongation.

V. STABILITY UNDER STATIC LOADING

Using the bend fixture system illustrated in Figure 1, specimens of both high-strength steel and high-strength aluminum (2024-T3) were stressed to their yield point and held in contact with an organic liquid for one week. Almost every item in Table I has been applied and there have been no instances of failure under static loading. This is in spite of the fact that the saline solution solvents produced obvious rusting of the steel specimens and fixtures.

TABLE I

CATALOGUE OF ORGANIC LIQUID CANDIDATES

Name	Solvent*	Concentration	Reference Code
	Organic Acids		
2-Ethylhexanoic acid		100%	A-1
n-Butyric acid		100%	A-2
	Saline water	Satd.	A-2-W
n-Oleic acid		100%	A-3
Stearic acid	Light paraffin oil	Satd.	A-4
	Dibutyl carbitol	1.5%	A-5
	Saline water	Satd.	A-4-W
Castor oil (Recinoleic acid)		100%	A-6
2,4,6-Trimethylbenzoic acid	Dibutyl carbitol	1.0%	A-7
	Saline water	Satd.	A-7-W
2,4,5-Triethoxybenzoic acid	Dibutyl carbitol	2.0%	A-8
2,4,6-Trinitrobenzoic acid	Dioctylphthalate	1.3%	A-9
	Saline water	Satd.	A-9-W
Triphenylacetic acid	Halocarbon oil	1.5%	A-10
	Saline water	Satd.	A-10-W
Bromoacetic acid	Dioctylphthalate	10%	A-11
	Saline water	Satd.	A-11-W
Crotonic acid	Dioctylphthalate	7.0%	A-12
	Saline water	Satd.	A-12-W
Lauric acid	Heavy white mineral oil	6.6%	A-13
Oxalic acid	Heavy mineral oil	1.0%	A-14
	Saline water	Satd.	A-14-W
Trichloroacetic acid	Saline water	Satd.	A-15
	Amines		
n-Butylamine		100%	B-1
	Dibutyl carbitol	50%	B-2
	Saline water	Satd.	B-1-W
tert-Butylamine	Saline water	Satd.	B-3-W
n-Hexylamine		100%	B-16
	Dibutyl carbitol	50%	B-4
	Saline water	Satd.	B-16-W
Dibenzylamine		100%	B-5

TABLE I (CONT'D)

Name	Solvent*	Concen-tration	Reference Code
m-Toluidine	Dioctylphthalate	50%	B-6
	Saline water	Satd.	B-6-W
o-Chloroaniline	Dioctylphthalate	50%	B-7
p-Nitroaniline	Dioctylphthalate	7.5%	B-8
	Saline water	Satd.	B-8-W
Phenylhydrazine		100%	B-9
	Saline water	Satd.	B-9-W
2,4-Dinitrophenylhydrazine	Dioctylphthalate	1.6%	B-10
	Saline water	Satd.	B-10-W
N,N-Dimethyl-o-toluidine	Heavy white mineral oil	10%	B-11
Cetyldimethylbenzyl ammonium chloride	Heavy white mineral oil	4.7%	B-12
	Saline water	Satd.	B-12-W
Benzyltrimethyl ammonium chloride	Water	61%	B-13
	Saline water	Satd.	B-13-W
Urea	Heavy mineral oil	0.5%	B-14
	Saline water	Satd.	B-14-W
tetra-n-Butyl ammonium iodide	Dioctylphthalate	4.0%	B-15
	Saline	Satd.	B-15-W
Triethyl ammonium chloride	Dioctylphthalate	3.0%	B-17
	Saline water	Satd.	B-17-W
Hydrazine hydrate	Saline water	Satd.	B-18-W
Melamine	Saline water	Satd.	B-19-W
Phenylenediamine	Saline water	Satd.	B-20-W
Phenylurea	Saline water	Satd.	B-21-W
Phenyl acetonitride	Saline water	Satd.	B-22-W
p-Amino diphenylamine	Saline water	Satd.	B-23-W
p-Phenylenediamine	Saline water	Satd.	B-24-W
p-Anisidine hydrochloride	Saline water	Satd.	B-25-W
trans-N,N,N',N'-tetramethyl-2-butene-1,4-diamine	Saline water	Satd.	B-26-W

TABLE I (CONT'D)

Name	Solvent*	Concentration	Reference Code
	Alcohol		
n-Butanol		100%	C-1
	Dibutyl carbitol	50%	C-2
Dibutyl carbitol		100%	C-3
2-Ethylhexanol		100%	C-4
	Saline water	Satd.	C-4-W
Cetyl alcohol	Light white paraffin oil	1.85%	C-5
Benzyl alcohol		100%	C-6
	Saline water	Satd.	C-6-W
o-Hydroxyphenol	Dioctylphthalate	3.3%	C-7
o-Methylphenol	Dioctylphthalate	50%	C-8
o-Nitrophenol	Dioctylphthalate	10%	C-9
	Saline water	Satd.	C-9-W
n-Butyl alcohol	Saline water	Satd.	C-10-W
Phenol	Saline water	Satd.	C-11-W
Picric acid	Saline water	Satd.	C-12-W
Catechol	Saline water	Satd.	C-13-W
	Metal Salts of Organic Acid		
Calcium Ricinoleate	Dioctylphthalate	4.0%	E-1
	Saline water	Satd.	E-1-W
Cadmium Ricinoleate	Dioctylphthalate	2.0%	E-2
	Saline water	Satd.	E-2-W
Zinc Ricinoleate	Heavy mineral oil	4.0%	E-3
	Saline water	Satd.	E-3-W
Nickel stearate	Heavy mineral oil	4.0%	E-4
	Saline water	Satd.	E-4-W
Magnesium stearate	Heavy mineral oil	4.0%	E-5
	Saline water	Satd.	E-5-W
Zinc acetate	Dioctylphthalate	5.0%	E-6
	Saline water	Satd.	E-6-W
Aluminum acetate	Dioctylphthalate	5.0%	E-7
	Saline water	Satd.	E-7-W
Chromium acetate	Dioctylphthalate	5.0%	E-8
	Saline water	Satd.	E-8-W

TABLE I (CONT'D)

Name	Solvent*	Concen-tration	Reference Code
Sodium stearate	Dioctylphthalate	5.0%	E-9
	Saline water	Satd.	E-9-W
Stannous oxalate	Dioctylphthalate	5.0%	E-10
	Saline water	Satd.	E-10-W
Potassium binoxalate	Dioctylphthalate	5.0%	E-11
	Saline water	Satd.	E-11-W
Sodium methyl silicone	Dioctylphthalate	5.0%	E-12
Lithium stearate	Dioctylphthalate	5.0%	E-13
	Saline water	Satd.	E-13-W
	Halogenated Organic Compounds		
Halocarbon oil		100%	G-1
	Organic Acid Amides		
N,N-Dimethylformamide	Halocarbon oil	33%	H-1
	Saline water	Satd.	H-1-W
	Hydrocarbon		
Heavy white mineral oil		100%	N-1
Light white paraffin oil		100%	N-2
	Ester		
Dioctylphthalate		100%	K-1
	Ketone		
Hydroquinone	Dioctylphthalate	2.2%	L-1
	Saline water	Satd.	L-1-W
	Organic Phosphorus, Sulfur, and Silicon Compounds		
Decane phosphoric acid	Dioctylphthalate	2.1%	M-1
	Saline water	Satd.	M-1-W
Diphenyl sulfane	Heavy white mineral oil	1.5%	M-2
	Saline water	Satd.	M-2-W
Dilauryl sulfane	Heavy white mineral oil	2.2%	M-3
Dimethyl sulfane		100%	M-4

TABLE I (CONT'D)

Name	Solvent*	Concen-tration	Reference Code
Triethyl phosphate	Saline water	Satd.	M-5
Tri-n-butyl phosphate	Saline water	Satd.	M-6-W
	Organic Ether		
Hexchlorodiphenyl oxide	Heavy mineral oil	1.1%	0.1
	Organic Ketoximes		
Dimethylglyoxime	Dibutyl carbitol	1.8%	P-1
	Saline water	Satd.	P-1-W
	Commercial Organic Surfactants		
Arlacel 165 emulsion	Heavy mineral oil	2.0%	Q-1
	Saline water	Satd.	Q-1-W
Lipal 4P emulsion	Heavy mineral oil	11.6%	Q-2
	Saline water	Satd.	Q-2-W
Benax 2A1 solution, 45% anionic		100%	Q-3
	Saline water	Satd.	Q-3-W
Tween 80		100%	Q-4
	Saline water	Satd.	Q-4-W
Pluronic L62		100%	Q-5
	Saline water	Satd.	Q-5-W
Maken NF-5		100%	Q-6
	Saline water	Satd.	Q-6-W
Tergitol NPX		100%	Q-7
	Saline water	Satd.	Q-7-W
Atlas G-672 Batch 9526-C		100%	Q-8
Solar TG-3440		100%	Q-9
	Saline water	Satd.	Q-9-W
Solar TG-2320		100%	Q-10
	Saline water	Satd.	Q-10-W
Dowfax 9N4		100%	Q-11
	Saline water	Satd.	Q-11-W
	Organic Acid Anhydride		
4-Nitrophthalic anhydride	Saline water	Satd.	R-1-W

TABLE I (CONT'D)

Name	Solvent*	Concen-tration	Reference Code
	Organic Metal Oxygen Compounds		
Sodium phenate	Dibutyl carbitol	2.0%	S-1
Sodium phenoxide	Saline water	Satd.	S-2-W
	Amines Organic Ether		
Ethoxylated stearylamine		100%	BO-1
	Saline water	Satd.	BO-1-W
	Amines Alcohol		
8-Hydroxyquinoline	Heavy mineral oil	2.5%	BC-1
	Saline water	Satd.	BC-1-W
o-Tolyl propanolamine	Saline water	Satd.	BC-2-W
Phenyl ethanolamine	Saline water	Satd.	BC-3-W
	Metal Organic Ester		
Dibutyl tin dilaurate		100%	FK-1
	Metal Organic Alcohol		
Triphenyl tin hydroxide	Dioctylphthalate	4.0%	FC-1
	Amines Ester		
Triethyl-2,4,6-triazine acetate	Saline water	Satd.	BK-1-W
	Alcohol Ketone		
Ninhydrin	Saline water	Satd.	LC-1-W
	Amines Aldehyde		
p-Dimethyl amino benzaldehyde	Saline water	Satd.	BD-1-W
	Silicon Metal Organic Compound		
Sodium methyl silicone	Saline water	Satd.	FM-1-W
	Sulfo-Metaloxy-Alcohol		
Zinc sulfocarbolate	Dioctylphthalate	5.0%	CMS-1
	Saline water	Satd.	CMS-1-W

* Saline water refers to 5.0% NaCl in water.

VI. FAILURE UNDER CYCLIC LOADING

Fatigue stressing has the special attribute of combining applied stress, slip (plastic strain), and cracking activity over a substantial period of time. Thus chemical interactions and surface-wetting processes involving the candidate surfactant liquids have considerable time to occur and to exert influence.

One describes fatigue failure by plotting the number of cycles to failure against the cyclic component of stress. This plot is commonly known as the S-N curve. Steel has the special attribute of an endurance limit--an alternating stress magnitude below which failure will never occur. Edge-notched sheet specimens with a filed 0.001 in. root radius have been tested in tension-tension fatigue. That is, a constant tensile stress is maintained on the specimen with a superimposed addition which cycles between zero and some maximum value. The S-N curve plotted in Figure 3 relates the magnitude of the cyclic maximum to the number of cycles to failure. There is a sharp and clearly defined endurance limit. The cracks originate from one or both of the edge notch roots and propagate in a direction transverse to the axis of stressing until the maximum stress exceeds the ultimate strength of the remaining cross section. About 50% of the total crack surface represents slowly advancing fatigue crack.

The action of a liquid environment is induced by clamping two liquid-saturated asbestos pads to the faces of the specimen over the whole notched area. A "Saran Wrap" envelope prevents volatilization. The solid points in Figure 3 demonstrate the ability of a simple 5% NaCl solution to depress the endurance limit and perhaps even to eliminate it. This is simple confirmation of previous Russian work.

As a basis for screening the effectiveness of a large number of organic liquid candidates, a single stress level has been chosen. This stress level is near but below the normal endurance limit. Thus a specimen dry and in air will not fail at this stress level even after millions of cycles. However, at this stress level, a 5% NaCl water solution will cause failure in 300,000-600,000 cycles. The effectiveness of other liquids can be judged by reference to these two comparative conditions. Table II summarizes the

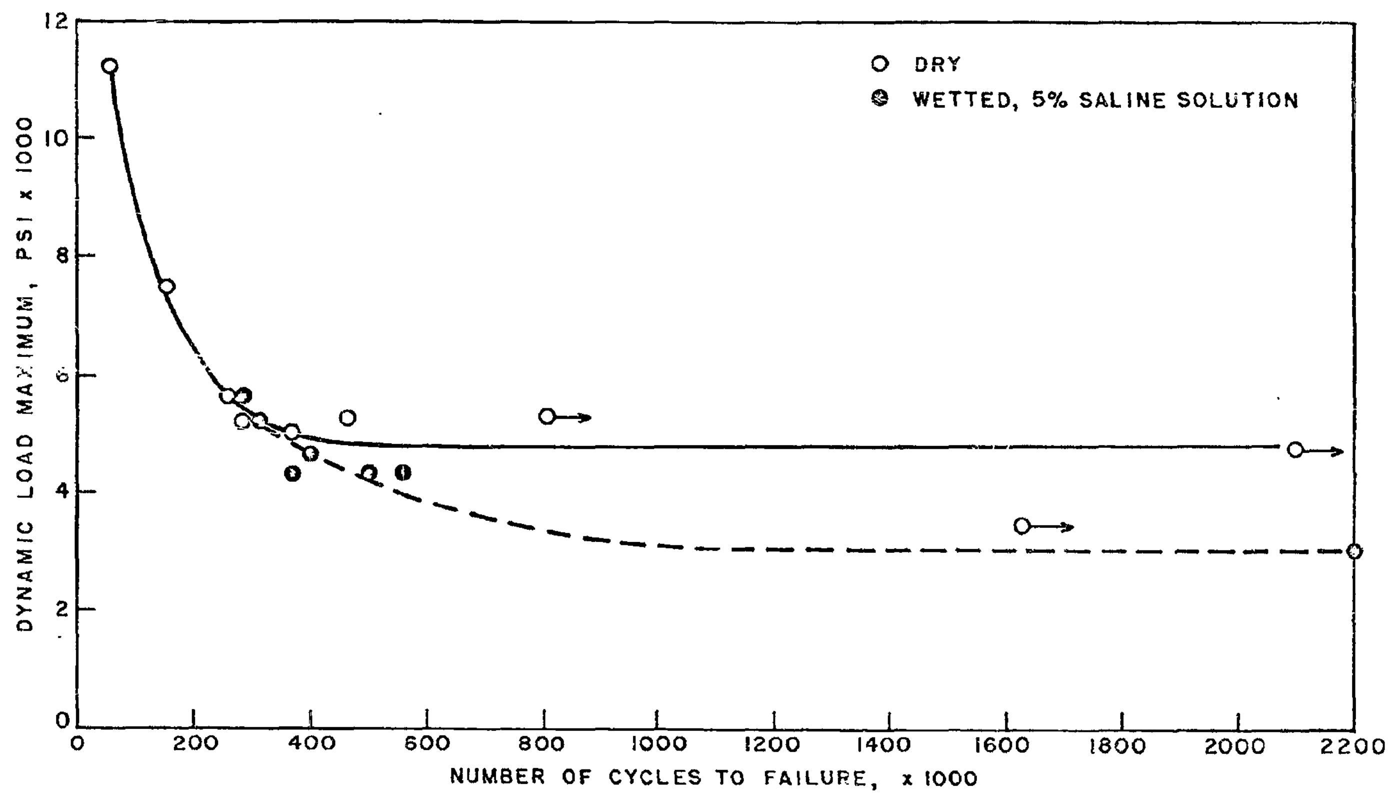


FIG. 3 - FATIGUE FAILURE OF 300M (HARDENED TO 200,000 PSI YIELD STRENGTH) UNDER A STATIC NOMINAL STRESS OF 12,500 PSI AND VARIABLE DYNAMIC NOMINAL STRESS AT 1,800 CPM.

TABLE II

FATIGUE STRENGTH OF HARDENED STEEL (300M) IN THE PRESENCE OF ORGANIC LIQUIDS

Organic Group	Organic Species	Test Cycles	Remarks
Alcohol	C-10-W	2,390,000	No failure
Organic acid	A-9-W	2,601,000	No failure
Metal salts of organic acids	E-1	797,000	No failure, no cracks
	E-1-W	558,000	Failure
	E-2	2,610,000	No failure, no cracks
	E-2-W	601,000	Failure
	E-3	2,530,000	No failure, no cracks
	E-3-W	495,000	Failure
	E-4	2,483,000	No failure, no cracks
	E-4-W	509,000	Failure
	E-5	2,561,000	No failure, no cracks
	E-5-W	666,000	Failure
Amines	B-10-W	392,000	Failure
	B-22-W	590,000	Failure
	B-22-W	858,000	Failure
Organic surfactants	Q-6-W	457,000	Failure
	Q-6-W	744,000	Failure
	Q-6-W	739,000	No failure, edge cracks
	Q-7-W	481,000	Failure
	Q-11-W	616,000	Failure
	Q-10-W	1,262,000	Failure
	Q-9-W	605,000	Failure
	Q-4-W	710,000	Failure
	Q-1-W	868,000	Failure
	Q-3-W	605,000	Failure
	Q-5-W	522,000	Failure
	Q-2-W	601,000	Failure

results of testing thus far. The simple conclusion that must be drawn is that organic liquids not containing water are inert and those containing a saline water solution generally are no more effective than the simple saline solution itself or somewhat less effective. This, of course, is the substance of the results thus far. A broader sample of potential candidates is necessary and the whole regimen of testing is yet to be applied to the Al 2024 alloy.

VII. PERSONNEL AND LOGBOOKS

The research program is under the supervision of the writer with technical consultation by Mr. R. H. Crouse, Senior Chemist. The work itself is being performed by Mr. H. Nichols, Associate Metallurgist, and Mr. R. Sarocco, Technician. The results reported are contained in ARF Logbooks No. 13011 and 13536.

Respectfully submitted,

ARMOUR RESEARCH FOUNDATION OF
ILLINOIS INSTITUTE OF TECHNOLOGY

W. Rostoker

W. Rostoker

Tech Rev: JFR

jw